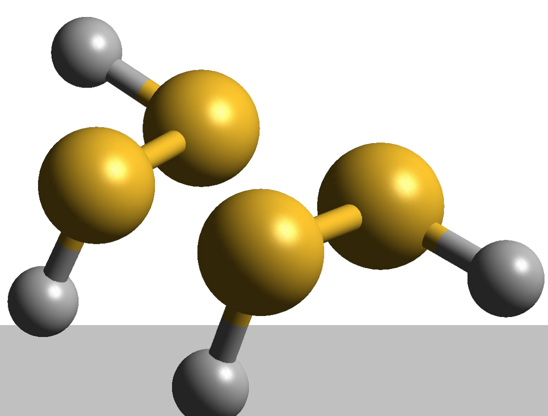
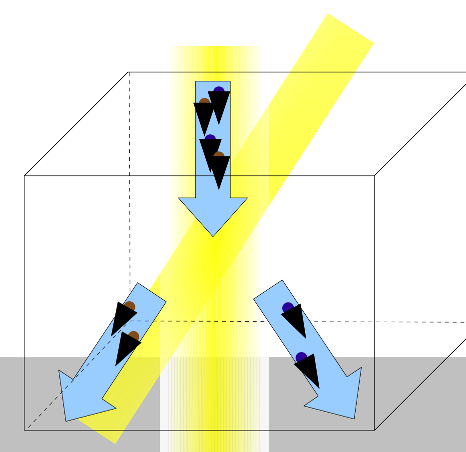
Rotational effects on enantioseparation

Andreas Jacob and Klaus Hornberger





Enantioseparation

Existing schemes based on:
- other chiral substances
- optical rotation

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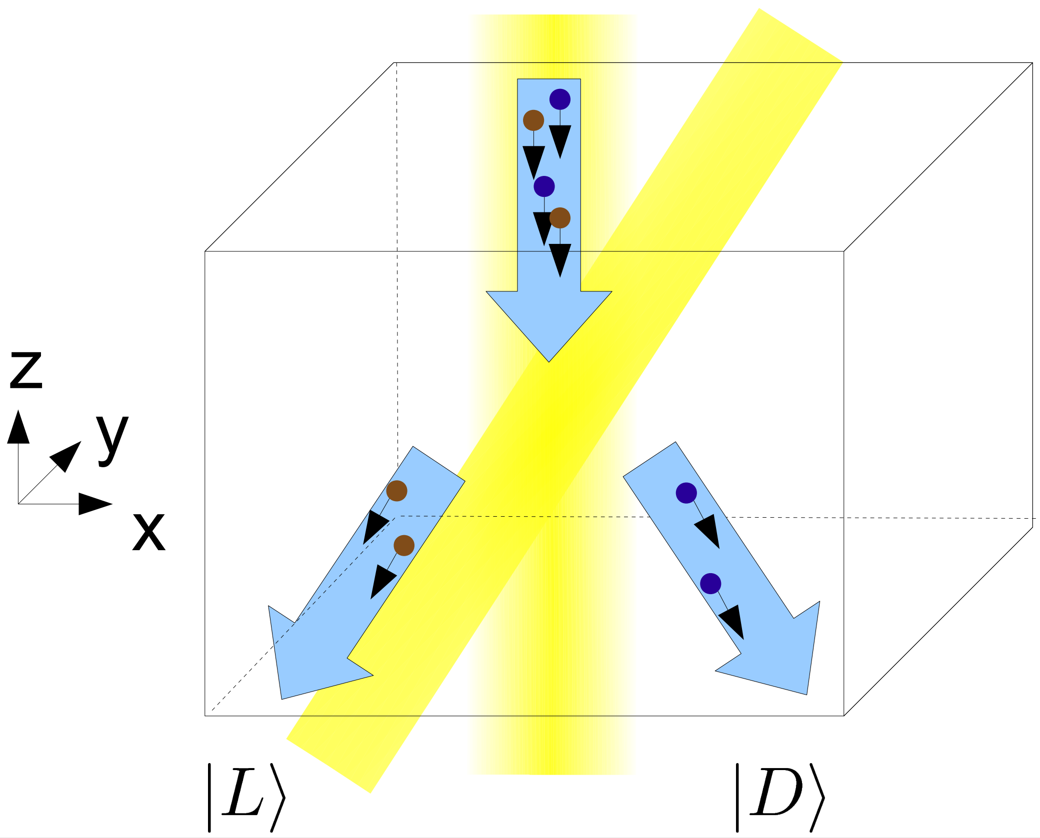
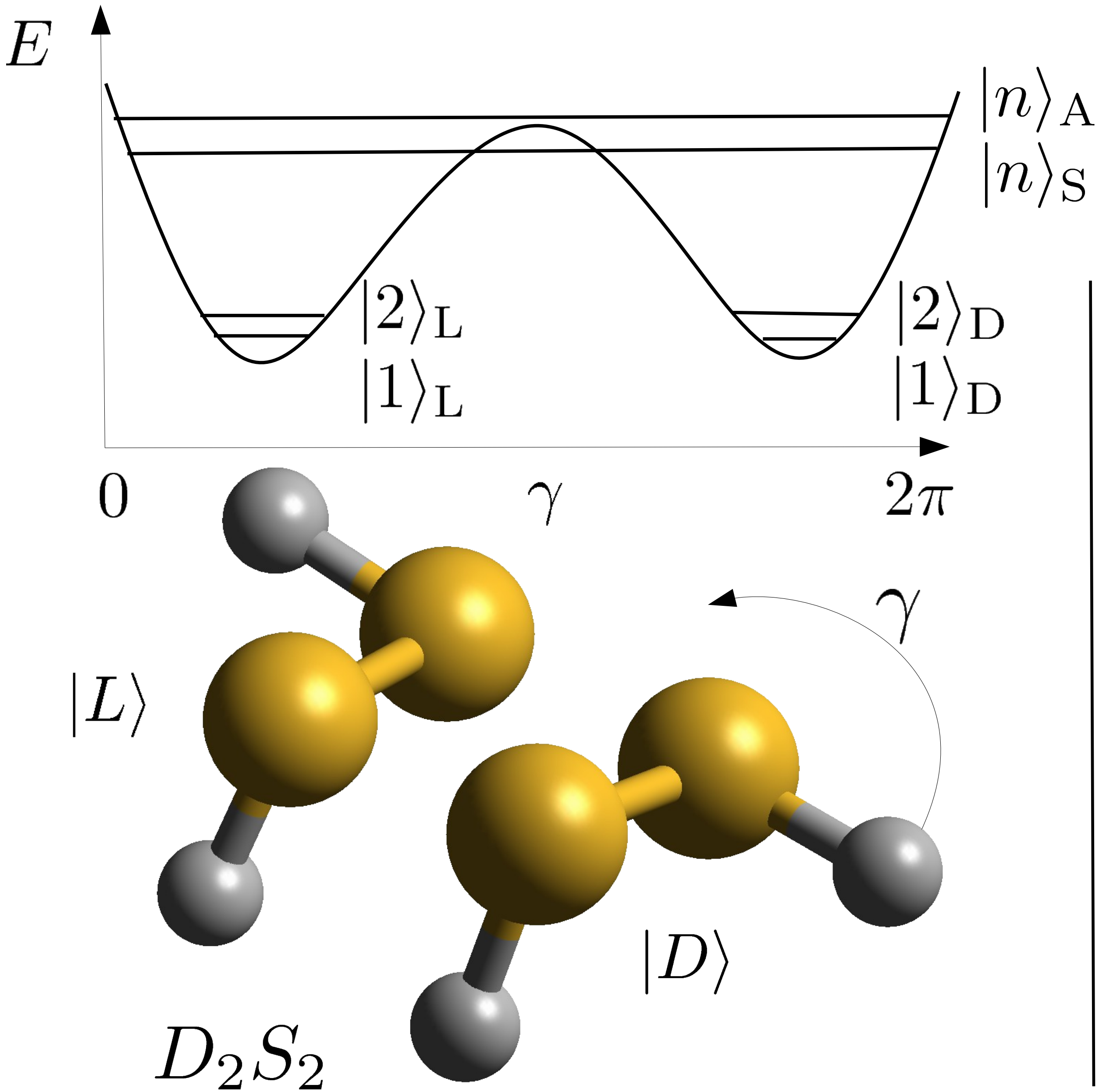
Goal:



Chiral Molecules



Eigenstates of the Hamiltionian

$$|S\rangle = \frac{1}{\sqrt{2}}\left(|D\rangle + |L\rangle\right)$$

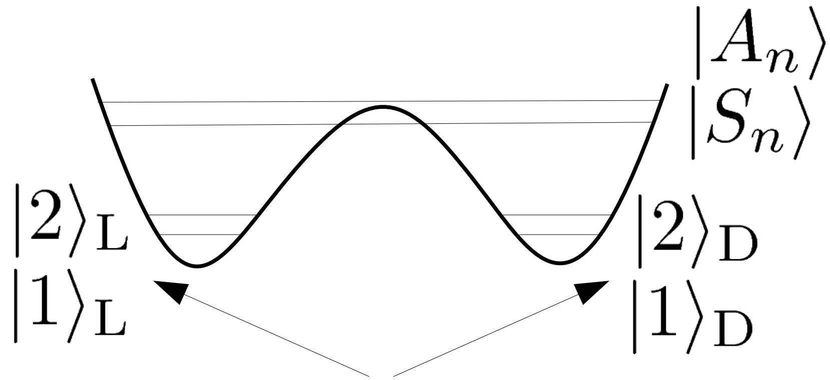
$$|A\rangle = \frac{1}{\sqrt{2}}\left(|D\rangle - |L\rangle\right)$$

but one observes

$$|L\rangle = \frac{1}{\sqrt{2}}\left(|S\rangle - |A\rangle\right)$$

$$|D\rangle = \frac{1}{\sqrt{2}}\left(|S\rangle + |A\rangle\right)$$

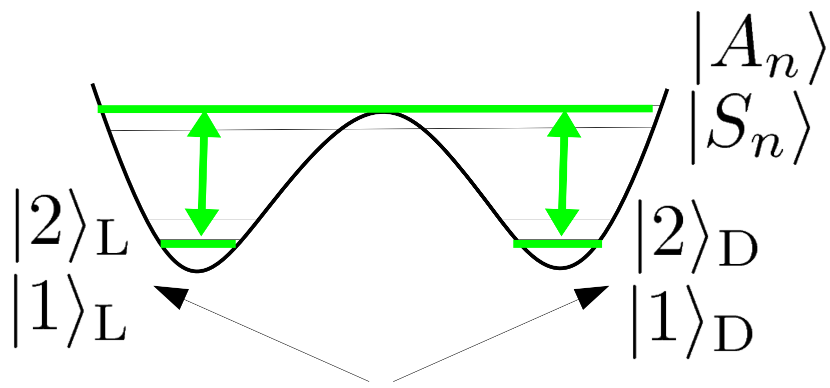
Basic Idea



$$|i^{\pm}\rangle \quad = \quad |S_i\rangle \pm |A_i\rangle$$

Shapiro and Brumer: Principles of the quantum control of molecular processes, Wiley(2003)

Basic Idea

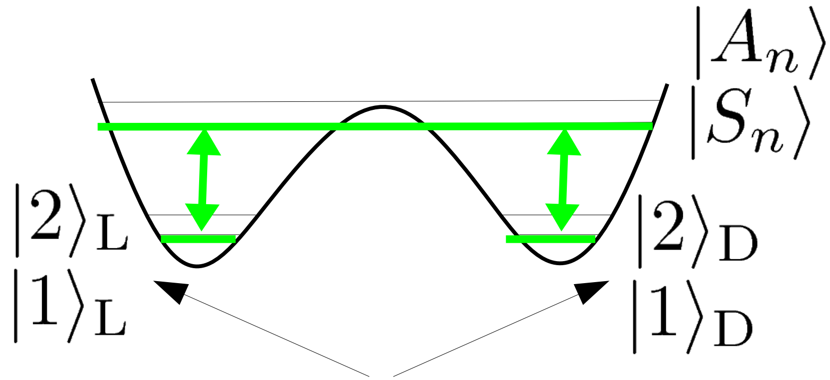


$$|i^{\pm}\rangle = |S_i\rangle \pm |A_i\rangle$$

asymmetric → chiral:

$$\begin{aligned}\Omega_{ij} &= \langle i^{\pm}|\mu|A_j\rangle E \\ &= \langle S_i|\mu|A_j\rangle E\end{aligned}$$

Basic Idea



$$|i^{\pm}\rangle = |S_i\rangle \pm |A_i\rangle$$

$$\text{asymmetric} \rightarrow \text{chiral: } \Omega_{ij} = \langle i^{\pm}|\mu|A_j\rangle E = \langle S_i|\mu|A_j\rangle E$$

$$\text{symmetric} \rightarrow \text{chiral: } \Omega_{ij} = \langle i^{\pm}|\mu|S_j\rangle E = \pm\langle A_i|\mu|S_j\rangle E$$

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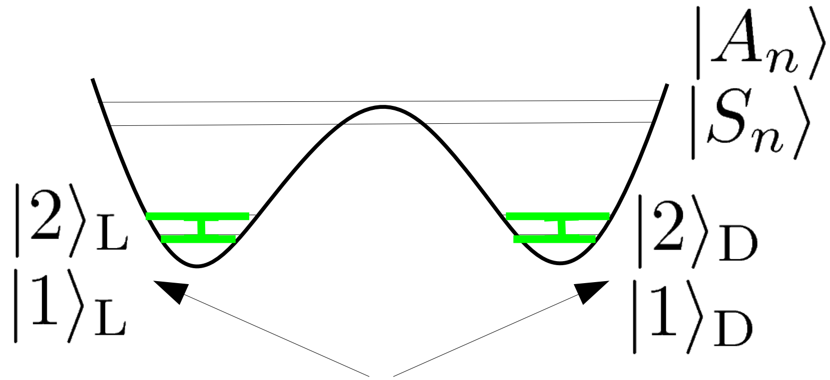
Basic Idea



$$|i^{\pm}\rangle = |S_i\rangle \pm |A_i\rangle$$

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&= \pm\langle A_i|\mu|S_j\rangle E
\end{aligned}$$

$$\begin{aligned}
\text{chiral} \rightarrow \text{chiral: } \Omega_{ij} &= \langle i^{\pm}|\mu|j^{\pm}\rangle E \\
&= \pm\left[\langle S_i|\mu|A_j\rangle + \langle A_i|\mu|S_j\rangle\right] E
\end{aligned}$$

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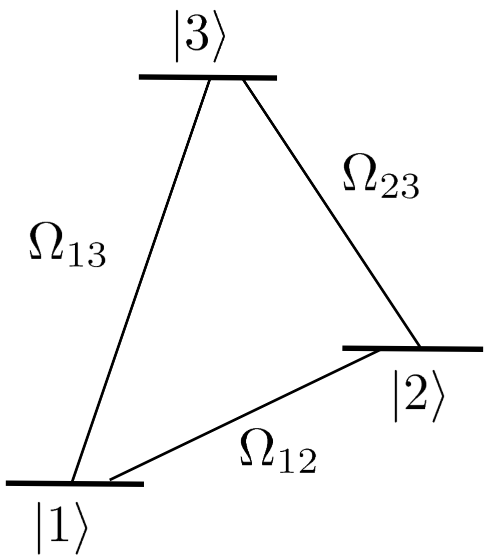
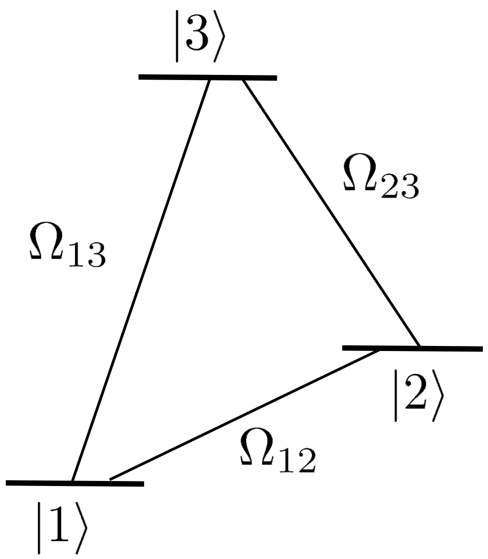
Closed Loop Scheme



$$\begin{aligned}\Omega_{12}^{D} &= -\Omega_{12}^{L}\\ \Omega_{13}^{D} &= -\Omega_{13}^{L}\\ \Omega_{23}^{D} &= -\Omega_{23}^{L}\end{aligned}$$

Closed Loop Scheme



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we can go to the basis of dressed states $|\chi_i\rangle$ and obtain effective equations of motion

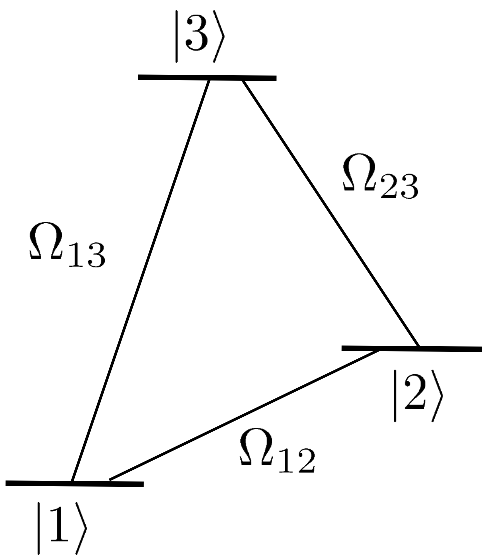
$$H = \frac{1}{2m}(\mathbf{p} - \mathbf{A})^2 + V(x, y) - mGz$$

$$\boldsymbol{A}_i(\boldsymbol{r}) = \mathrm{i}\hbar\langle\chi_i(\boldsymbol{r})|\boldsymbol{\nabla}|\chi_i(\boldsymbol{r})\rangle$$

$$V_i(\boldsymbol{r}) = \lambda_i(\boldsymbol{r}) + \langle\chi_i(\boldsymbol{r})|U(\boldsymbol{r})|\chi_i(\boldsymbol{r})\rangle$$

Li and Shapiro. J. Chem. Phys. **132**, 194315 (2010)

Closed Loop Scheme



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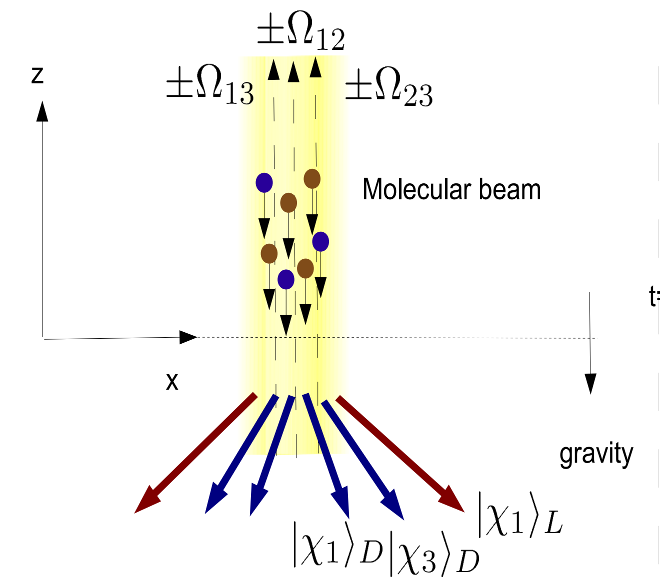
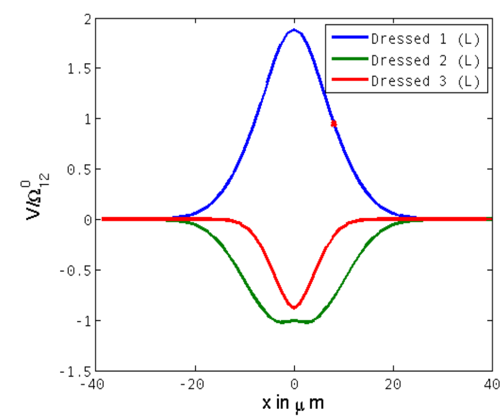
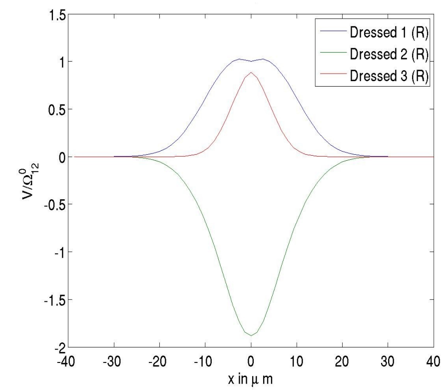
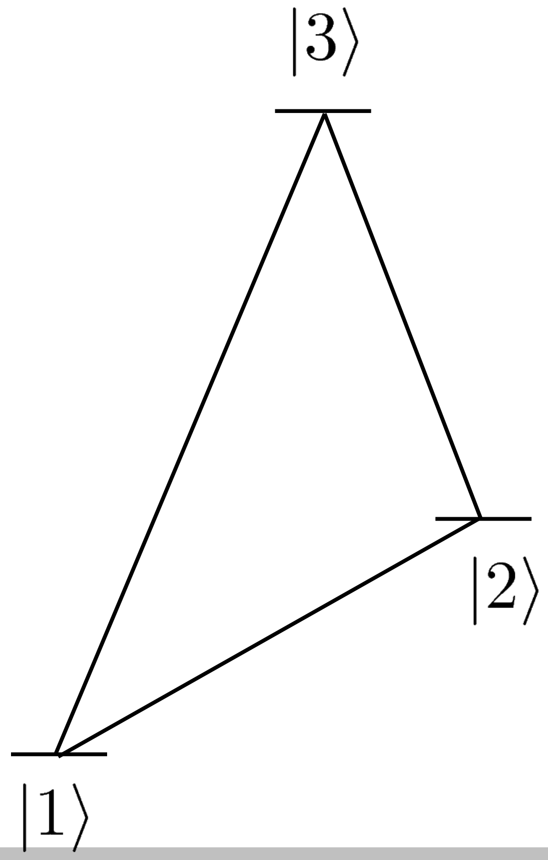






Effects of molecular rotation

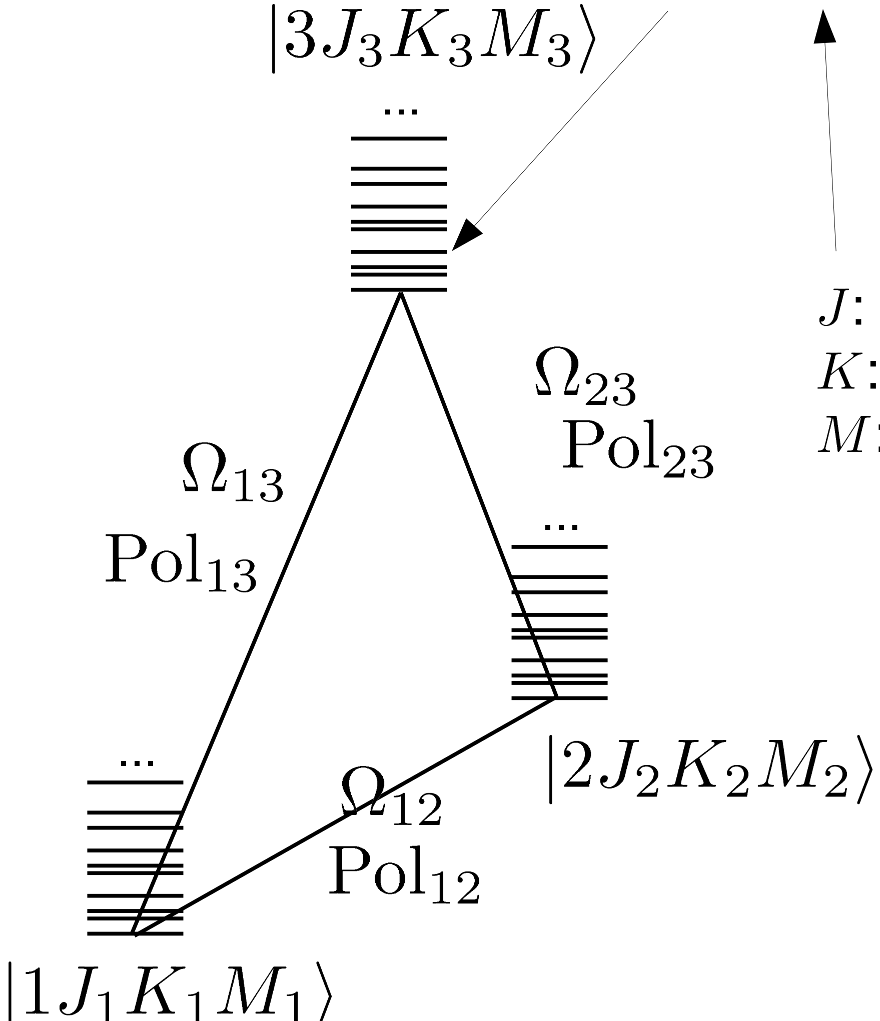


Effects of molecular rotation

molecule modelled e.g. as symmetric top:

$$E\left(J,K,M_J\right) \quad = \quad hcBJ\left(J+1\right)+hc\left(A-B\right)K^2$$

A^{-1}, B^{-1}: moments of inertia



J: rotational quantum number

K: helicity, projection of $\mathbf{J}$ onto molecular axis, $-J\ldots J$

M: projection of $\mathbf{J}$ onto space fixed axis, $-J\ldots J$

Selection Rules

$$\Omega = \langle \Psi_2 | \boldsymbol{\mu} \cdot \mathbf{E} | \Psi_1 \rangle$$

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transform dipole moment from molecular frame (M) to lab frame (S)

$$\boldsymbol{\mu} \cdot \boldsymbol{E} = \sum_{\sigma=\{\pm 1,0\}} \mu_\sigma^S E_\sigma^S \qquad \mu_\sigma^S = \sum_{\sigma'=-1}^{1} D^1_{\sigma'\sigma}(\alpha\beta\gamma)\, \mu^M_{\sigma'}$$

$$= \sum_{\sigma'=\{\pm 1,0\}} \sum_{\sigma=\{\pm 1,0\}} D^1_{\sigma'\sigma}(\alpha\beta\gamma)\, \mu^M_{\sigma'} E^S_\sigma$$

Selection Rules

$$\Omega = \langle \Psi_2 | \boldsymbol{\mu} \cdot \mathbf{E} | \Psi_1 \rangle$$

$$|\Psi_1\rangle = |\Psi^{J_1}_{K_1 M_1}\rangle \otimes |\nu_1\rangle$$

transform dipole moment from molecular frame (M) to lab frame (S)

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Selection Rules

$$\Omega = \langle \Psi_2 | \boldsymbol{\mu} \cdot \mathbf{E} | \Psi_1 \rangle$$

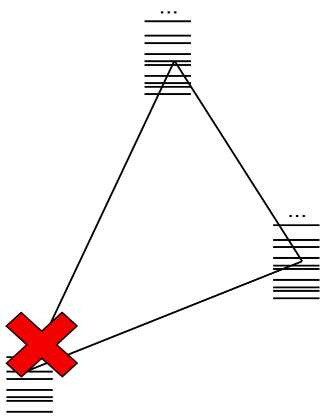
$$= \langle \nu_2 | \otimes \langle \Psi^{J_2}_{K_2 M_2} | \sum_{\sigma' = \{\pm 1, 0\}} \sum_{\sigma = \{\pm 1, 0\}} D^1_{\sigma' \sigma} \mu^M_{\sigma'} E^S_\sigma | \Psi^{J_1}_{K_1 M_1} \rangle \otimes | \nu_1 \rangle$$

$$= \sum_{\sigma' = \{\pm 1, 0\}} \langle \nu_2 | \mu^M_{\sigma'} | \nu_1 \rangle \sum_{\sigma = \{\pm 1, 0\}} \langle \Psi^{J_2}_{K_2 M_2} | D^1_{\sigma' \sigma} | \Psi^{J_1}_{K_1 M_1} \rangle E^S_\sigma$$

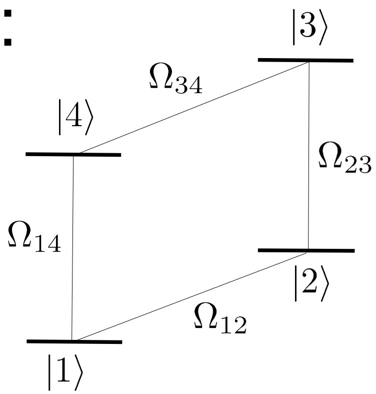
$$= \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} D^{J_2}_{K_2 M_2} (\theta \phi \chi) \, D^1_{\sigma', \sigma} (\theta \phi \chi) D^{J_1}_{K_1 M_1} (\theta \phi \chi) \sin \theta \mathrm{d}\theta \mathrm{d}\phi \mathrm{d}\chi$$

Results

* rotational selection rules do **not** allow loops involving 3 levels.



* an even number of levels is conceivable:



* But: an even number of levels yields an even number of different Ωs in both enantiomers
  - **control of chirality is lost**

Summary & Outlook

* The potentials from the adiabatic dressed states approach are **not** recovered if molecular rotations are included

* transitions other than the electric dipole transition might be applied (multipole transitions, opt. angular momentum, ...)

* optimal control helps to find
  - optimal spatial profile E(x)
  - optimal timing E(t)

  of laser
  with the objective to maximize the separation